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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a lamination type piezo electric crystal ceramic device, especially the lamination type piezo electric crystal ceramic device obtained by really calcinating an internal electrode and a piezo electric crystal ceramic layer.

[0002]

[Description of the Prior Art]Conventionally, the piezo electric crystal ceramics which use lead zirconate titanate (hereafter referred to as PZT) as the main ingredients are widely known by the piezo electric crystal used for an actuator, a transformer, etc.

There are some which lay an internal electrode underground in these piezo electric crystal ceramics, and are used as a lamination type piezo electric crystal ceramic device as that structure.

[0003]As piezo electric crystal ceramics which use such PZT as the main ingredients, For a piezoelectric property improvement, replace a part of Pb by Ca, Sr, and Ba, or, The compound perovskite type oxide of three component systems which become $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3$ and $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is used well. Ag or an Ag-Pd alloy is used as an internal electrode used when laminating the piezo electric crystal ceramics which use PZT as the main ingredients.

[0004]In generally producing the above-mentioned lamination type piezo electric crystal ceramic device, the slurry obtained by mixing the charge of a piezo electric crystal ceramic material and binder which consist of temporary-quenching powder first is fabricated to a sheet shaped, and it is considered as a green sheet. Next, after printing an internal electrode paste so that it may become a desired pattern, and sticking these by pressure on this green sheet,

the method of really calcinating a green sheet and an internal electrode paste is taken.

[0005]

[Problem(s) to be Solved by the Invention]However, when the charge of a piezo electric crystal ceramic material and the internal electrode were made to really calcinate as mentioned above and the lamination type piezo electric crystal ceramic device was obtained, there was a problem that especially the mechanical quality factor Q_m changed with the differences among laminated structures, such as a number of layers of a layered product and thickness per layer.

[0006]Even if the purpose of this invention has a difference in laminated structures, such as a number of layers of a layered product, and thickness per layer, there is in providing the lamination type piezo electric crystal ceramic device which can control change of the mechanical quality factor Q_m .

[0007]

[Means for Solving the Problem]This invention is made in view of the above purposes. A lamination type piezo electric crystal ceramic device of an invention of this application 1st, Pb element which is a lamination type piezo electric crystal ceramic device which comes to laminate a piezo electric crystal ceramic layer and an internal electrode layer, and said piezo electric crystal ceramic layer has a Perovskite type crystal structure expressed with ABO_3 , and contains to A site, Zr element and Ti elements which are contained to B site, and Cr elements as a trivalent element contained to B site, Among Na as a monad of A site, and K, among Ca as dyad of at least one sort and A site, Ba, and Sr At least one sort, Among La as a trivalent element of A site, Nd, and Bi, at least one sort, Among Sn as tetrad of B site, Nb as pentad of B site, Sb, and Ta, at least one sort, And in [consist of piezo electric crystal ceramics containing at least one sort of elements chosen from W as a hexad of B site, and] said piezo electric crystal ceramics, It is $\text{zeta} = [(A_3 - A_1) + \{(2 \times B_6) + B_5 - B_3\}] \times e$ (C) about a gap of an electric charge to an equilibrium situation when A site is made divalent and B site is made into tetravalence.

however, a time of setting a total of B site elements to $1 - A_1$: -- the total mole ratio of a monad of said A site. The total mole ratio of a trivalent element of an A_3 :aforementioned A site, B_3 :

The total mole ratio of a trivalent element of said B site, The total mole ratio of pentad of a B_5 :aforementioned B site, B_6 : When it is defined as the total mole ratio of a hexad of said B

site, and e:elementary charge (1.60×10^{-19} (C)), zeta/e is characterized by being $0.017 \leq \text{zeta}/e \leq 0.028$.

[0008]Even if a laminated structure has a difference by using the above presentations, a rate of change of the mechanical quality factor Q_m can be controlled within 35%.

[0009]A lamination type piezo electric crystal ceramic device of an invention of this application

2nd is characterized by ζ/e in a lamination type piezo electric crystal ceramic device of the 1st invention being $0.021 \leq \zeta/e \leq 0.028$.

[0010] Even if a laminated structure has a difference by using the above presentations, a rate of change of the mechanical quality factor Q_m can be controlled within 25 more%.

[0011] A lamination type piezo electric crystal ceramic device of an invention of this application

3rd, It is a lamination type piezo electric crystal ceramic device which comes to laminate a piezo electric crystal ceramic layer and an internal electrode layer, Pb element which said piezo electric crystal ceramic layer has a Perovskite type crystal structure expressed with ABO_3 , and contains to A site, Among Co as Zr element and Ti elements which are contained to B site, and dyad contained to B site, nickel, and Mg, at least one sort of elements, Among Na as a monad of A site, and K, among Ca as dyad of at least one sort and A site, Ba, and Sr At least one sort, Among La as a trivalent element of A site, Nd, and Bi, at least one sort, Among Sn as tetrad of B site, Nb as pentad of B site, Sb, and Ta, at least one sort, and W as a hexad of B site and ***** -- it consisting of one sort of elements, and piezo electric crystal ceramics to contain, even if small, and in said piezo electric crystal ceramics, It is $\zeta = [(A_3 - A_1) + \{(2 \times B_6) + B_5 - (2 \times B_2)\}] \times e$ (C) about a gap of an electric charge to an equilibrium situation

when A site is made divalent and B site is made into tetravalence.

however, a time of setting a total of B site elements to $1 - A_1$: -- the total mole ratio of a monad of said A site. The total mole ratio of a trivalent element of an A_3 :aforementioned A site, B_2 :

The total mole ratio of dyad of said B site, The total mole ratio of pentad of a

B_5 :aforementioned B site, B_6 : When it is defined as the total mole ratio of a hexad of said B

site, and e:elementary charge (1.60×10^{-19} (C)), ζ/e is characterized by being $0.008 \leq \zeta/e \leq 0.017$.

[0012] Even if a laminated structure has a difference by using the above presentations, a rate of change of the mechanical quality factor Q_m can be controlled within 35%.

[0013] A lamination type piezo electric crystal ceramic device of an invention of this application

4th is characterized by ζ/e in a lamination type piezo electric crystal ceramic device of the 3rd invention being $0.012 \leq \zeta/e \leq 0.017$.

[0014] Even if a laminated structure has a difference by using the above presentations, a rate of change of the mechanical quality factor Q_m can be controlled within 25 more%.

[0015]

[Embodiment of the Invention] Hereafter, the lamination type piezo electric crystal ceramic device of this invention is explained. This invention is characterized by a lamination type piezo electric crystal ceramic device comprising the following.

Piezo electric crystal ceramic layer.

Internal electrode layer.

Exterior electrodes.

The internal electrode layer is laid under the piezo electric crystal ceramic layer, and is pulled out by the side or the end face of the lamination type piezo electric crystal ceramic device. The internal electrode connected to different polarity may be pulled out to a field different, respectively, and it may pull out on the same field. In the case of the latter, exterior electrodes will be formed so that it may become independent electrically on [two] the same side. Exterior electrodes are formed in the end face thru/or the side of a lamination type piezo electric crystal ceramic device, and are electrically connected with the internal electrode. The shape and the formation position of exterior electrodes should just be determined according to the mounting configuration of the electronic parts, and are not limited in particular.

[0016]The piezo electric crystal ceramics which constitute the piezo electric crystal ceramic layer in the lamination type piezo electric crystal ceramic device of this invention are using PbTiO_3 - PbZrO_3 as the main ingredients, and have a Perovskite type crystal structure.

Although A/B cannot be limited to 1 which is a stoichiometric ratio and it can be made to change suitably if needed, being referred to as 0.97-1.03 is preferred. Among these, the element chosen from Na as a monad, K, La as a trivalent element, Nd, and Bi may replace Pb which hits A site.

[0017]Zr and Ti which hit B site are replaced by the element of Cr as Co, nickel, Mg, or the trivalent element as dyad, and also Sn as tetrad, Nb as pentad, Sb, Ta, and the element chosen from W as a hexad may replace them. However, in order to suppress the rate of change of the mechanical quality factor (Q_m) by the difference in a laminated structure to 35% or less, when it replaces including Cr as a trivalent element, When A site is replaced including Co as dyad, nickel, and Mg so that zeta/e when divalent and B site are considered as tetravalence may be set to 0.017-0.028, A site must be replaced so that zeta/e when divalent and B site are considered as tetravalence may be set to 0.008-0.017. When it is in a mentioned range and Sb is not included as pentad of B site, the rate of change of the above-mentioned mechanical quality factor (Q_m) can stop even to 25%.

[0018]When zeta/e is in the range of 0.021-0.028 in the former and zeta/e is in the range of 0.012-0.017 in the latter, Though Sb is included as pentad of a metaphor B site, the rate of change of the mechanical quality factor (Q_m) by the difference in a laminated structure is suppressed to 25% or less, and is still more preferred. The gap zeta of an electric charge here refers to a gap of the electric charge between the above-mentioned element groups, and an equilibrium situation refers to the state of the gap zeta= 0 of this electric charge. That is, though elements other than the above-mentioned element group were added, since it is not directly related to the effect of this invention, no elements other than the above-mentioned element group shall be considered as an element which has on the gap zeta of an electric

charge.

[0019] Although elements, such as Mn and Fe, are generally added by piezo electric crystal ceramics or inevitable impurities, such as Si, aluminum, and Cl, are contained in them, these elements may be contained to such an extent that it does not have an adverse effect on piezoelectric property, such as an electromechanical coupling coefficient. The internal electrode composing element which really diffused the inevitable impurity here in the piezo electric crystal ceramic layer by calcination, and its content point out the element below 200 ppm of the whole piezoelectric ceramic.

[0020] The internal electrode layer in the lamination type piezo electric crystal ceramic device of this invention is laid underground between piezo electric crystal ceramic layers, and it comes to sinter it with piezo electric crystal ceramics in one. As for the presentation, Ag, Pd, Pt, an Ag-Pd alloy, Ag-Pt alloy, etc. are mentioned. Since the melting point of Ag is as low as about 960 **, depending on the presentation of ceramics, the direction of the sintering temperature of ceramics will become high. Therefore, it is preferred to use an Ag-Pd alloy with the higher melting point.

[0021]

[Example] Hereafter, the lamination type piezo electric crystal ceramic device and lamination type piezo electric crystal ceramic electronic component of this invention are explained still more concretely.

(Example 1) The following were first prepared as a starting material.

- (1) PbO , ZrO_2 , TiO_2 (main ingredients)
- (2) Na_2O , K_2O (compound of the monad included in A site)
- (3) CaCO_3 , BaCO_3 , SrCO_3 (compound of the dyad included in A site)
- (4) La_2O_3 , Nd_2O_3 , Bi_2O_3 (compound of the trivalent element included in A site)
- (5) Cr_2O_3 (compound of the trivalent element included in B site)
- (6) SnO_2 (compound of the tetrad included in B site)
- (7) Nb_2O_5 , Sb_2O_3 , Ta_2O_5 (compound of the pentad included in B site)
- (8) WO_3 (compound of the hexad included in B site)

As these were shown in Tables 1-4 in general formula (I), weighing of each starting material was carried out, and it was considered as piezo electric crystal material.

$(\text{Pb}_{\alpha} \text{O}_3 (\text{Zr}_x \text{Ti}_y \text{beta}_z) \dots (I)$

(Elements other than elements other than Pb by which alpha goes into A site, Zr by which beta goes into B site, and Ti, $x+y+z=1$)

After adding pure water and carrying out wet blending with a ball mill about each piezo electric

crystal material, it was made to dry and dry and was considered as powder mixture.

[0022]Next, temporary quenching of the obtained powder mixture was carried out at 800-1000 **, and temporary-quenching powder was obtained. After having added a binder, a dispersing agent, a surface-active agent, a defoaming agent, pure water, etc. to the obtained temporary-quenching powder, mixing and considering it as slurry form, it was considered as the green sheet with the doctor blade method.

[0023]the obtained green sheet -- an internal electrode -- public funds -- what was screen-stenciled so that it might become a pattern of a request of the internal electrode paste which contains the Ag-Pd alloy of Ag: Pd=70:30 as group powder was accumulated and stuck by pressure, and it was considered as the layered product. Two kinds, what was made into the internal electrode of three layers and the distance between internal electrodes of 180 micrometers (layered product 1), and the thing (layered product 2) made into internal electrode two-layer and 370 micrometers of inter electrode distances, were produced. Next, the obtained layered product was calcinated at 1080-1200 **, and the sintered compact was obtained. After grinding the both principal planes of this sintered compact and forming an electrode, the poling process was performed in 60-150 ** insulation oil. Then, 150-280 ** heat treatment was added, it cut so that the bottom might serve as a square which are 15 mm x 15 mm, and it was considered as the lamination type piezo electric crystal ceramic device. The gap zeta of the electric charge in each sample was computed by the following formulas, and zeta/e was shown in Tables 1 and 2.

$$\text{zeta} = [(A_3 - A_1) + \{(2 \times B_6) + B_5 - B_3\}] \times e \quad (C)$$

When the total of B site elements is set to 1. Mole-ratio [of the hexad of the total mole-ratio B_6 :B site of the pentad of the total mole-ratio B_5 :B site of the trivalent element of the total mole-ratio B_3 :B site of the trivalent element of the total mole-ratio A_3 :A site of the monad of an A_1 :A site / total] e: Elementary charge (1.60×10^{-19} (C))

The mechanical quality factor Qm of the lamination type piezo electric crystal ceramic device produced by performing it above was measured with the impedance analyzer, the mechanical quality factor Qm of the layered product 1 and the layered product 2 was compared, and the rate of change (%) was computed. The rate of change of the mechanical quality factor Qm was computed based on the following formulas.

[0024]

[Formula 1]

$$\text{Qm変化率} = \left| \frac{(\text{積層体 1 の Qm}) - (\text{積層体 2 の Qm})}{(\text{積層体 2 の Qm})} \times 100 \right| (\%)$$

[0025]The result is shown in Tables 3 and 4.

[0026]

[Table 1]

試料 番号	Aサイト										Bサイト										ζ/ρ								
	1価	2価 ^w					3価	総量 ($\times 10^{-2}$ mol)	Zr x	Ti y	z																		
	($\times 10^{-2}$ mol)										($\times 10^{-3}$ mol)																		
	Na	K	Ca	Ba	Sr	La	Nd		Bi	Co	Ni	Mg	Cr	Sn	Nb	Sb	Te	W											
	($\times 10^{-2}$) mol										($\times 10^{-3}$) mol											($\times 10^{-3}$) mol							
*1	100.0	—	—	—	—	—	—	—	100.0	45.6	49.0	—	—	—	2.08	—	3.33	—	—	—	—	—	0.013						
*2	100.0	—	—	—	—	—	—	—	100.0	46.0	49.0	—	—	—	1.67	—	3.33	—	—	—	—	—	0.017						
3	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.25	—	3.33	—	—	—	—	—	0.021						
4	100.0	—	—	—	—	—	—	—	100.0	47.1	49.0	—	—	—	0.54	—	3.33	—	—	—	—	—	0.028						
*5	100.0	—	—	—	—	—	—	—	100.0	46.7	49.0	—	—	—	0.54	—	3.75	—	—	—	—	—	0.032						
*6	100.0	—	—	—	—	—	—	—	100.0	46.0	49.0	—	—	—	2.08	—	0.83	0.83	0.83	0.83	0.42	0.013	0.013						
*7	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.67	—	0.83	0.83	0.83	0.83	0.42	0.017	0.017						
8	100.0	—	—	—	—	—	—	—	100.0	46.8	49.0	—	—	—	1.25	—	0.83	0.83	0.83	0.42	0.021	0.021	0.021						
9	100.0	—	—	—	—	—	—	—	100.0	47.5	49.0	—	—	—	0.54	—	0.83	0.83	0.83	0.83	0.42	0.028	0.028						
*10	100.0	—	—	—	—	—	—	—	100.0	47.1	49.0	—	—	—	0.54	—	0.97	0.97	0.97	0.97	0.42	0.032	0.032						
11	100.0	—	—	—	—	—	—	—	100.0	46.8	49.0	—	—	—	1.25	—	1.25	1.25	—	—	—	—	0.021	0.021					
12	100.0	—	—	—	—	—	—	—	100.0	46.8	49.0	—	—	—	1.25	—	1.25	1.25	—	—	—	—	0.021	0.021					
13	100.0	—	—	—	—	—	—	—	100.0	46.8	49.0	—	—	—	1.25	—	1.25	1.25	—	—	—	—	0.021	0.021					
14	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.25	—	1.11	1.11	—	—	—	—	0.021	0.021					
15	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.25	—	1.67	1.67	—	—	—	—	0.021	0.021					
16	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.25	—	1.67	1.67	—	—	—	—	0.021	0.021					
17	100.0	—	—	—	—	—	—	—	100.0	47.3	49.0	—	—	—	1.25	—	1.67	—	—	—	—	—	0.021	0.021					
18	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.25	—	1.67	1.67	—	—	—	—	0.021	0.021					
19	100.0	—	—	—	—	—	—	—	100.0	47.3	49.0	—	—	—	1.25	—	1.67	—	—	—	—	—	0.021	0.021					
*20	100.0	—	—	—	—	—	—	—	100.0	45.6	49.0	—	—	—	2.08	—	—	—	—	—	—	—	0.013	0.013					
*21	100.0	—	—	—	—	—	—	—	100.0	46.0	49.0	—	—	—	1.67	—	—	—	—	—	—	—	0.017	0.017					
22	100.0	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	1.25	—	—	—	—	—	—	—	0.021	0.021					
23	100.0	—	—	—	—	—	—	—	100.0	46.8	49.0	—	—	—	0.83	—	—	—	—	—	—	—	0.025	0.025					
24	100.0	—	—	—	—	—	—	—	100.0	47.1	49.0	—	—	—	0.54	—	—	—	—	—	—	—	0.028	0.028					
*25	100.0	—	—	—	—	—	—	—	100.0	46.7	49.0	—	—	—	0.54	—	—	—	—	—	—	—	0.032	0.032					

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*印は請求項3の範囲外

[0027]

[Table 2]

試料 番号	Aサイト										Bサイト										ζ/e		
	1価		2価		3価						総量 ($\times 10^{-2}$ mol)	Zr x ($\times 10^{-2}$ mol)	Y y ($\times 10^{-2}$ mol)	z									
	$(\times 10^{-2} \text{mol})$													$(\times 10^{-2} \text{mol})$									
	Na	K	Ca	Ba	Sr	La	Nd	Bi	Co	Ni				Mg	Cr	Sn	Nb	Sb	Ta	W			
26	100.0	—	—	—	—	—	—	—	—	100.0	46.4	49.0	—	—	—	—	1.25	—	—	—	3.33	—	0.021
27	100.0	—	—	—	—	—	—	—	—	100.0	48.1	49.0	—	—	—	—	1.25	—	—	—	—	1.67	0.021
28	98.0	0.40	0.40	—	—	—	0.40	0.40	0.40	100.0	45.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.021
※29	98.0	0.40	0.40	—	—	—	0.40	0.40	0.40	100.0	47.1	49.0	—	—	—	—	0.54	—	3.33	—	—	—	0.032
30	98.0	—	0.80	—	—	—	0.40	0.40	0.40	100.0	45.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.021
31	98.0	0.40	0.40	—	—	—	1.20	—	—	100.0	46.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.021
32	99.0	—	—	—	—	—	0.33	0.33	0.33	100.0	46.4	49.0	—	—	—	—	1.67	—	2.92	—	—	—	0.023
33	98.0	0.80	—	—	—	—	1.20	—	—	100.0	45.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.021
34	98.0	—	0.80	—	—	—	1.20	—	—	100.0	46.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.021
35	99.5	0.50	—	—	—	—	—	—	—	100.0	45.8	49.0	—	—	—	—	0.83	—	3.33	—	—	—	0.020
36	99.5	—	0.50	—	—	—	—	—	—	100.0	45.8	49.0	—	—	—	—	0.83	—	3.33	—	—	—	0.020
37	99.5	—	—	—	—	—	0.50	—	—	100.0	45.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.022
38	99.5	—	—	—	—	—	—	0.50	—	100.0	45.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.022
39	99.5	—	—	—	—	—	—	—	0.50	100.0	46.0	49.0	—	—	—	—	1.67	—	3.33	—	—	—	0.022
40	98.0	—	0.67	0.67	—	—	—	—	—	100.0	46.4	49.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
41	99.0	—	1.00	—	—	—	—	—	—	100.0	45.4	49.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
42	99.0	—	—	1.00	—	—	—	—	—	100.0	45.4	49.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
43	99.0	—	—	—	1.00	—	—	—	—	100.0	46.4	49.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
44	100.0	—	—	—	—	—	—	—	—	100.0	44.4	49.0	—	—	—	—	1.25	2.00	3.33	—	—	—	0.021
45	98.0	—	—	—	—	—	—	—	—	98.0	46.4	49.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
46	102.0	—	—	—	—	—	—	—	—	102.0	46.4	49.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
47	100.0	—	—	—	—	—	—	—	—	100.0	48.4	47.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021
48	100.0	—	—	—	—	—	—	—	—	100.0	44.4	51.0	—	—	—	—	1.25	—	3.33	—	—	—	0.021

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[0028]

[Table 3]

試料 番号	焼成 温度 (°C)	特 性		
		積層体1の Qm (%)	積層体2の Qm (%)	Qm 変化率 (%)
※1	1100	215	156	38
*2	1100	170	142	20
3	1120	129	115	12
4	1140	96	90	7
※5	1200	—	—	離脱結
※6	1080	270	186	45
*7	1080	216	164	32
8	1100	176	142	24
9	1140	127	113	12
※10	1200	—	—	離脱結
11	1100	145	123	18
12	1100	172	154	12
13	1100	200	164	22
14	1140	143	123	16
15	1140	174	144	21
16	1140	175	156	12
17	1100	146	124	18
18	1140	181	147	23
19	1100	202	163	24
※20	1100	266	180	49
*21	1120	215	163	32
22	1140	175	142	23
23	1140	139	118	18
24	1160	96	86	12
※25	1200	—	—	離脱結

※印は本発明の範囲外
*印は請求項3の範囲外

[0029]

[Table 4]

試料 番号	焼成 温度 (°C)	特 性		
		積層体1の Qm (%)	積層体2の Qm (%)	Qm 変化率 (%)
26	1120	179	156	15
27	1100	224	190	18
28	1100	209	187	12
※29	1200	—	—	離脱結
30	1100	179	158	13
31	1120	189	162	12
32	1080	158	134	18
33	1100	171	147	18
34	1100	164	143	18
35	1100	188	166	12
36	1120	198	172	18
37	1120	151	136	11
38	1120	152	133	14
39	1100	139	124	12
40	1140	162	145	12
41	1120	182	159	15
42	1120	177	157	13
43	1120	187	164	14
44	1100	170	152	12
45	1140	164	144	14
46	1100	189	163	16
47	1120	164	145	13
48	1120	202	180	12

※印は本発明の範囲外

[0030]As shown in Tables 1-4, it turns out that the rate of change of the mechanical quality

factor [that / to which the lamination type piezo electric crystal ceramic device produced using the above-mentioned element has zeta/e in the range of 0.017-0.028 regardless of the combination and composition ratio] Qm between two kinds of layered products is less than 35%.

[0031]It turns out that the rate of change of the above-mentioned mechanical quality factor Qm has satisfied 25% or less further what has zeta/e in the range of 0.021-0.028.

[0032]On the other hand, since the rate of change of the mechanical quality factor Qm between two kinds of layered products becomes larger than 35% like the sample numbers 1, 6, and 20 when zeta/e is smaller than 0.017 (i.e., when the gap of an electric charge to an equilibrium situation is too small), it is not desirable. Like the sample numbers 5, 10, and 25, when zeta/e is larger than 0.028 (i.e., when the gap of an electric charge to an equilibrium situation is too large), since it becomes difficult to sinter the piezo electric crystal ceramics themselves, it is not desirable.

[0033]Although it is within the limits of this invention, about the sample numbers 2, 7, and 21 from which zeta/e has separated from the range of 0.021-0.028, the sample number 2 which does not contain Sb is removed and the rate of change of the mechanical quality factor Qm between two kinds of layered products is larger than 25%.

(Example 2) The following were first prepared as a starting material.

- (1) PbO, ZrO₂, TiO₂ (main ingredients)
- (2) Na₂O, K₂O (compound of the monad included in A site)
- (3) CaCO₃, BaCO₃, SrCO₃ (compound of the dyad included in A site)
- (4) La₂O₃, Nd₂O₃, Bi₂O₃ (compound of the trivalent element included in A site)
- (5) CoCO₃, NiO, Mg(OH)₂ (compound of the dyad included in B site)
- (6) SnO₂ (compound of the tetrad included in B site)
- (7) Nb₂O₅, Sb₂O₃, Ta₂O₅ (compound of the pentad included in B site)
- (8) WO₃ (compound of the hexad included in B site)

Hereafter, two kinds of lamination type piezo electric crystal ceramic devices were obtained like Example 1. The gap zeta of the electric charge in each sample was computed using the following formulas, and zeta/e was shown in Tables 5 and 6.

$$\text{zeta} = [(A_3 - A_1) + \{(2 \times B_6) + B_5 - (2 \times B_2)\}] \times e \quad (C)$$

When the total of B site elements is set to 1. Mole-ratio [of the hexad of the total mole-ratio B₆:B site of the pentad of the total mole-ratio B₅:B site of the dyad of the total mole-ratio B₂:B site of the trivalent element of the total mole-ratio A₃:A site of the monad of an A₁:A site / total]

e: Elementary charge (1.60×10^{-19} (C))

Next, the acquired rate of change of the mechanical quality factor Q_m of a lamination type piezo electric crystal ceramic device and the mechanical quality factor Q_m was measured and computed like Example 1. The result is shown in Tables 7 and 8.

[0034]

[Table 5]

試料 番号	Aサイト										Bサイト										ζ/e																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
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※49	100.0	—	—	—	—	—	—	—	—	100.0	46.0	49.0	1.67	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

※印は本表明の範囲外
*印は請求項4の範囲外

[0035]

[Table 6]

試料 番号	Aサイト										Bサイト										Σ/e					
	1価					2価					3価					4価										
	$(\times 10^{-2} \text{ mol})$										Zr x $(\times 10^{-2} \text{ mol})$					Ti y $(\times 10^{-2} \text{ mol})$						Z $(\times 10^{-4} \text{ mol})$				
	Pb v (mol)	Na	K	Ca	Ba	Sr	La	Nd	Bi		Co	Ni	Mg	Cr	Sr	Nb	Sb	Ta	W							
74	100.0	—	—	—	—	—	—	—	—	100.0	46.6	49.0	1.04	—	—	—	—	3.33	—	0.013						
75	100.0	—	—	—	—	—	—	—	—	100.0	48.3	49.0	1.04	—	—	—	—	—	1.67	0.013						
76	100.0	—	—	—	—	—	—	—	—	100.0	46.6	49.0	—	1.04	—	—	3.33	—	—	0.013						
77	100.0	—	—	—	—	—	—	—	—	100.0	46.6	49.0	—	—	1.04	—	3.33	—	—	0.013						
78	100.0	—	—	—	—	—	—	—	—	100.0	46.6	49.0	0.35	0.35	0.35	—	3.33	—	—	0.013						
79	98.0	0.40	0.40	—	—	—	0.40	0.40	0.40	100.0	46.4	49.0	0.83	—	—	—	3.33	—	—	0.012						
80	98.0	0.40	0.40	—	—	—	0.40	0.40	0.40	100.0	46.8	49.0	0.83	—	—	—	3.33	—	—	0.021						
81	98.0	—	0.80	—	—	—	0.40	0.40	0.40	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.012						
82	98.0	0.40	0.40	—	—	—	1.20	—	—	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.012						
83	99.0	—	—	—	—	—	0.33	0.33	0.33	100.0	46.8	49.0	1.25	—	—	—	2.92	—	—	0.014						
84	98.0	0.80	—	—	—	—	1.20	—	—	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.012						
85	98.0	—	0.80	—	—	—	1.20	—	—	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.012						
86	99.5	0.50	—	—	—	—	—	—	—	100.0	46.8	49.0	0.83	—	—	—	3.33	—	—	0.012						
87	99.5	—	0.50	—	—	—	—	—	—	100.0	46.8	49.0	0.83	—	—	—	3.33	—	—	0.012						
88	99.5	—	—	—	—	—	0.50	—	—	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.013						
89	99.5	—	—	—	—	—	—	—	—	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.013						
90	99.5	—	—	—	—	—	—	—	0.50	100.0	46.4	49.0	1.25	—	—	—	3.33	—	—	0.013						
91	98.0	—	—	0.67	0.67	0.67	—	—	—	100.0	46.6	49.0	1.04	—	—	—	3.33	—	—	0.013						
92	99.0	—	—	1.00	—	—	—	—	—	100.0	46.6	49.0	1.04	—	—	—	3.33	—	—	0.013						
93	99.0	—	—	—	1.00	—	—	—	—	100.0	46.6	49.0	1.04	—	—	—	3.33	—	—	0.013						
94	99.0	—	—	—	—	1.00	—	—	—	100.0	46.6	49.0	1.04	—	—	—	3.33	—	—	0.013						
95	100.0	—	—	—	—	—	—	—	—	100.0	44.6	49.0	1.04	—	—	—	2.00	3.33	—	0.013						
96	98.0	—	—	—	—	—	—	—	—	98.0	46.6	49.0	1.04	—	—	—	—	3.33	—	0.013						
97	102.0	—	—	—	—	—	—	—	—	102.0	46.6	49.0	1.04	—	—	—	—	3.33	—	0.013						
98	100.0	—	—	—	—	—	—	—	—	100.0	48.6	47.0	1.04	—	—	—	—	3.33	—	0.013						
99	100.0	—	—	—	—	—	—	—	—	100.0	44.6	51.0	1.04	—	—	—	—	3.33	—	0.013						

※印は本発明の範囲外

※印は本発明の範囲外

[0036]

[Table 7]

試料 番号	焼成 温度 (℃)	特 性		Qm 変化率 (%)
		積層体1の Qm (%)	積層体2の Qm (%)	
※49	1100	506	368	38
*50	1120	234	195	20
51	1140	161	145	11
52	1160	130	123	6
※53	1180	—	—	離脱結
※54	1080	693	402	45
*55	1100	283	213	33
56	1120	169	136	24
57	1140	128	114	12
※58	1160	—	—	離脱結
59	1120	190	158	20
60	1120	164	144	14
61	1120	183	165	11
62	1140	141	125	13
63	1140	185	142	16
64	1140	178	159	12
65	1120	171	147	16
66	1140	147	129	14
67	1120	165	139	19
※68	1100	631	457	38
*69	1100	385	301	28
70	1160	268	225	19
71	1120	154	135	14
72	1140	120	110	9
※73	1180	—	—	離脱結

※印は本発明の範囲外

*印は請求項4の範囲外

[0037]

[Table 8]

試料 番号	焼成 温度 (℃)	特 性		Qm 変化率 (%)
		積層体1の Qm (%)	積層体2の Qm (%)	
74	1120	154	133	15
75	1100	177	154	15
76	1100	300	254	18
77	1120	136	113	20
78	1140	208	167	11
79	1140	231	196	18
※80	1180	—	—	離脱結
81	1100	190	165	15
82	1120	216	186	17
83	1100	146	123	19
84	1120	177	164	15
85	1120	170	145	17
86	1120	188	166	13
87	1120	237	215	10
88	1120	208	186	12
89	1120	228	193	18
90	1100	238	203	17
91	1140	182	168	15
92	1120	186	165	13
93	1120	168	147	14
94	1120	164	144	14
95	1120	175	156	12
96	1120	168	145	16
97	1100	185	158	17
98	1140	141	126	12
99	1140	213	187	14

※印は本発明の範囲外

[0038]As shown in Tables 5-8, it turns out that the rate of change of the mechanical quality factor Q_m [that / to which the lamination type piezo electric crystal ceramic device produced using the above-mentioned element has ζ/e in the range of 0.008-0.017 regardless of the combination and composition ratio] Q_m between two kinds of layered products is less than 35%.

[0039]It turns out that the rate of change of the mechanical quality factor Q_m has satisfied 25% or less further what has ζ/e in the range of 0.012-0.017.

[0040]On the other hand, since the rate of change of the mechanical quality factor Q_m between two kinds of layered products becomes larger than 35% like the sample numbers 49, 54, and 68 when ζ/e is smaller than 0.012 (i.e., when the gap of an electric charge to an equilibrium situation is too small), it is not desirable. Like the sample numbers 53, 58, 73, and 80, when ζ/e is larger than 0.017 (i.e., when the gap of an electric charge to an equilibrium situation is too large), since it becomes difficult to sinter the piezo electric crystal ceramics themselves, it is not desirable.

[0041]Although it is within the limits of this invention, about the sample numbers 50, 55, and 69 from which it has separated from the range of claim 4, the sample number 50 which does not contain Sb is removed and the rate of change of the mechanical quality factor Q_m between two kinds of layered products is larger than 25%.

[0042]

[Effect of the Invention]When a gap of the electric charge which the lamination type piezo electric crystal ceramic device of this invention contains Cr elements to the piezo electric crystal ceramics which constitute a piezo electric crystal ceramic layer, and the piezo electric crystal ceramic layer has is set to ζ , Since it is the presentation which shifted ζ/e from the equilibrium situation to the 0.017 to 0.028-minute donor side, the rate of change of the mechanical quality factor Q_m by the difference in a laminated structure is made to 35% or less.

[0043]The rate of change of the mechanical quality factor Q_m by the difference in a laminated structure is made to 25% or less by considering it as the presentation which shifted above-mentioned ζ/e from the equilibrium situation to the 0.021 to 0.028-minute donor side.

[0044]The lamination type piezo electric crystal ceramic device of this invention, When a gap of the electric charge which contains at least one sort of elements among Co, nickel, or Mg to the piezo electric crystal ceramics which constitute a piezo electric crystal ceramic layer, and the piezo electric crystal ceramic layer has is set to ζ , Since ζ/e serves as a presentation shifted to the 0.008 to 0.017-minute donor side from the equilibrium situation, the rate of change of the mechanical quality factor Q_m by the difference in a laminated structure is made to 35% or less.

[0045]The rate of change of the mechanical quality factor Q_m by the difference in a laminated structure is made to 25% or less by considering it as the presentation which shifted above-mentioned ζ/ϵ from the equilibrium situation to the 0.012 to 0.017-minute donor side.

[Translation done.]